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**Rathsack**

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(54) **MULTI-STEP BAKE APPARATUS AND METHOD FOR DIRECTED SELF-ASSEMBLY LITHOGRAPHY CONTROL**

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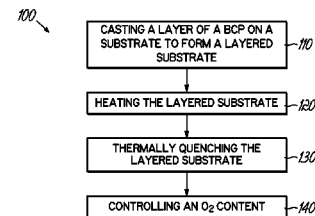
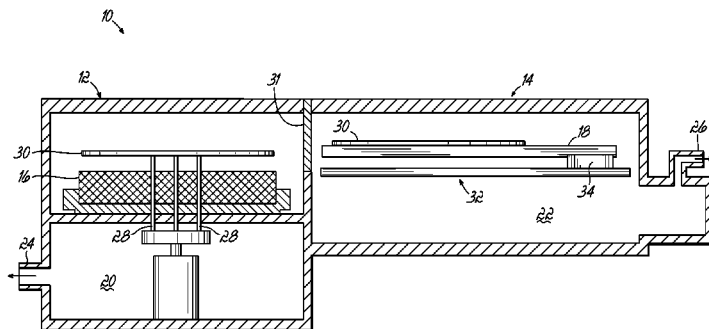
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(57) **ABSTRACT**

A method of forming a patterned substrate includes casting a layer of a block copolymer having an intrinsic glass transition temperature  $T_g$ , on a substrate to form a layered substrate. The method also includes heating the layered substrate at an annealing temperature, which is greater than about 50° C. above the intrinsic glass transition temperature  $T_g$  of the block copolymer, in a first atmosphere. The method further includes thermally quenching the layered substrate to a quenching temperature lower than the intrinsic glass transition temperature  $T_g$ , at a rate of greater than about 50° C./minute in a second atmosphere. The method further includes controlling an oxygen content in the first and second atmospheres to a level equal to or less than about 8 ppm to maintain the annealing and quenching temperatures below a thermal degradation temperature  $T_d$  of the block copolymer.

**20 Claims, 4 Drawing Sheets**



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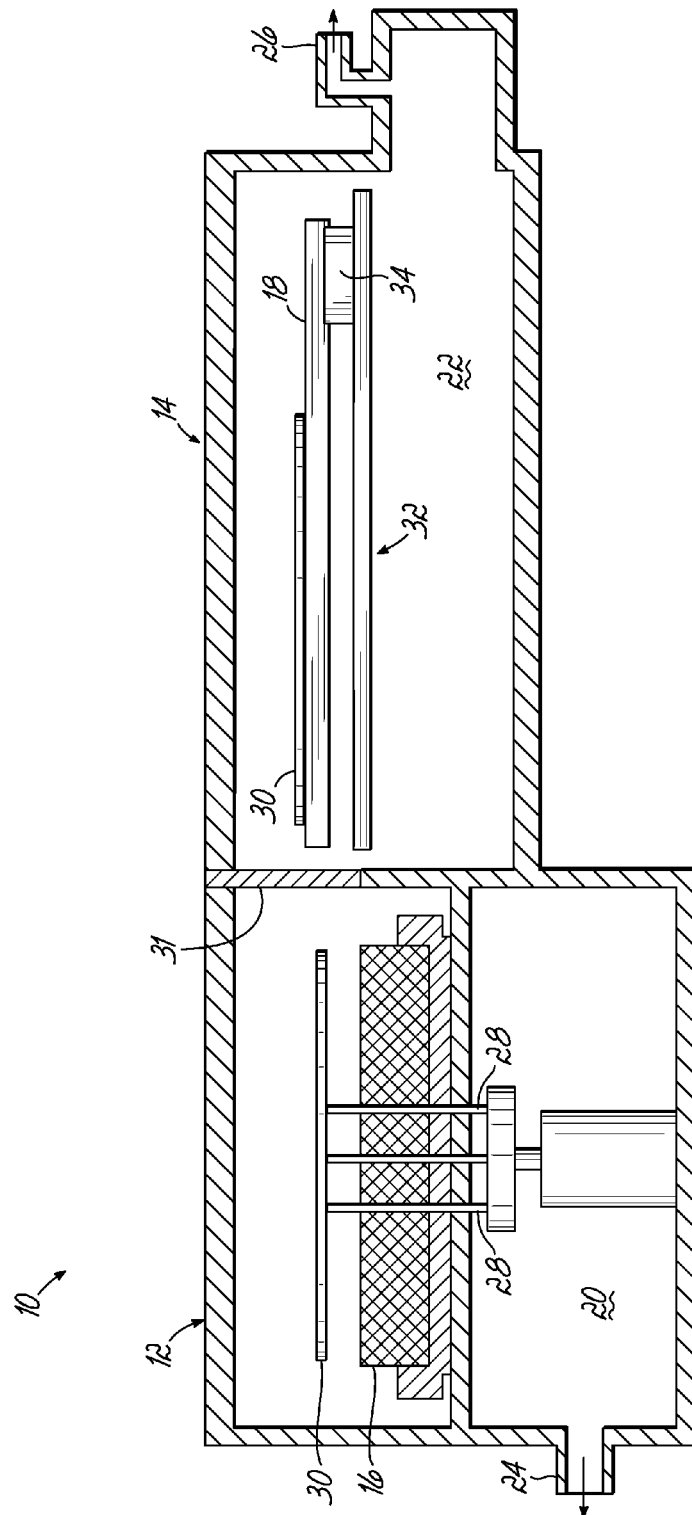


FIG. 1A

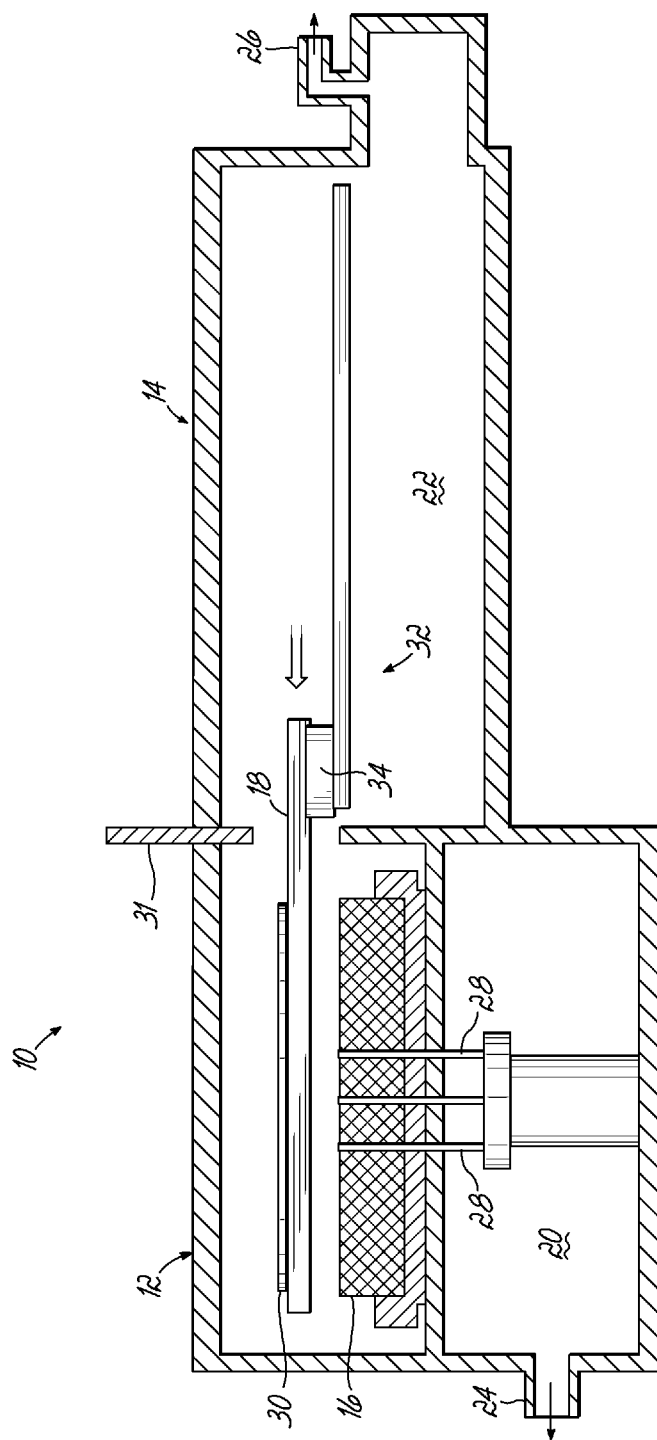


FIG. 1B

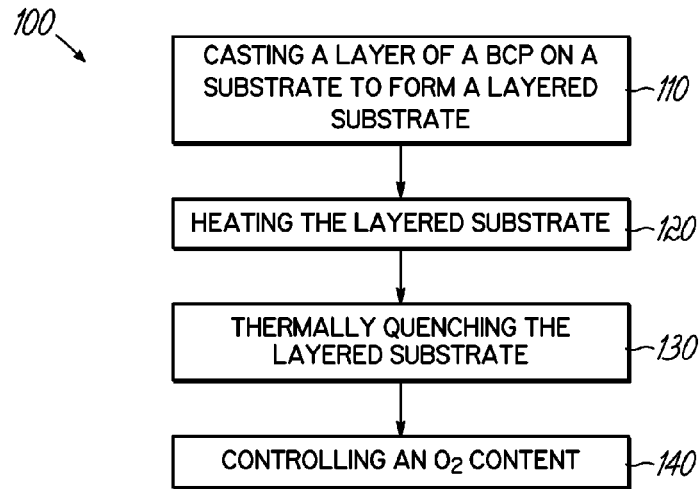


FIG. 2

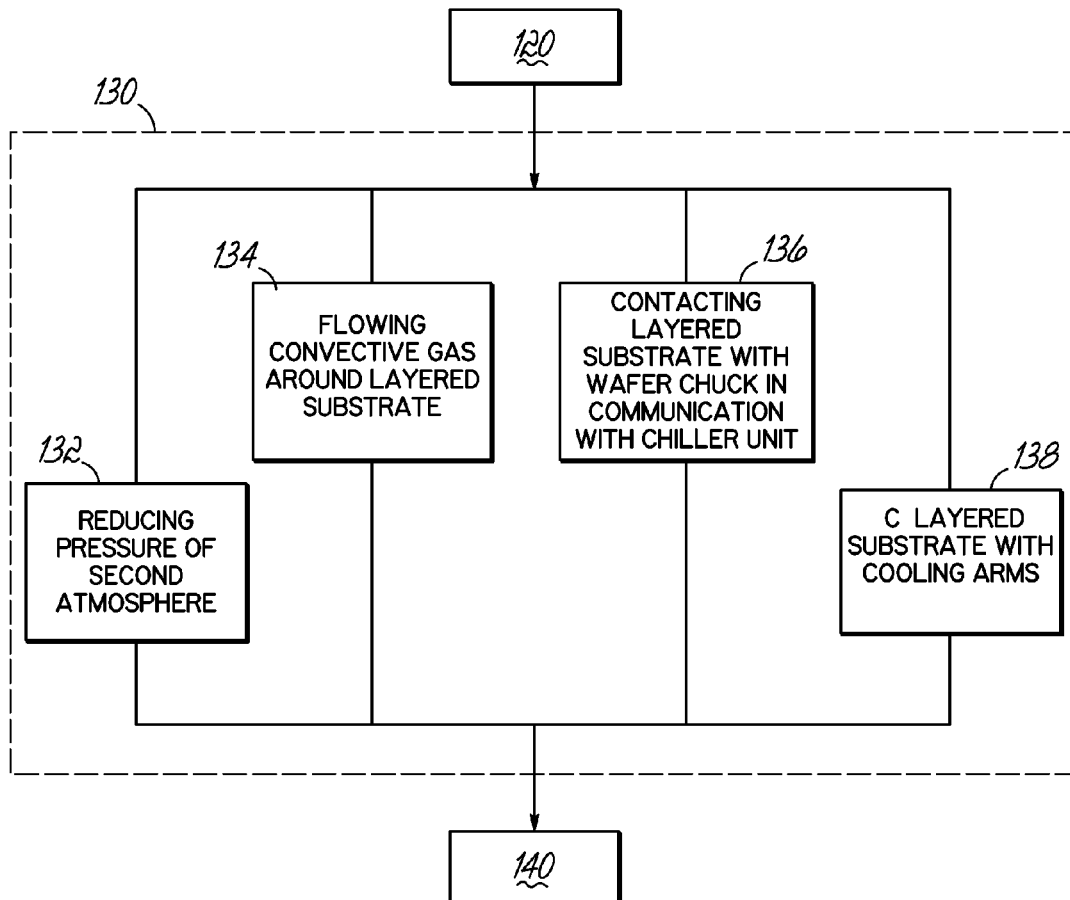


FIG. 3

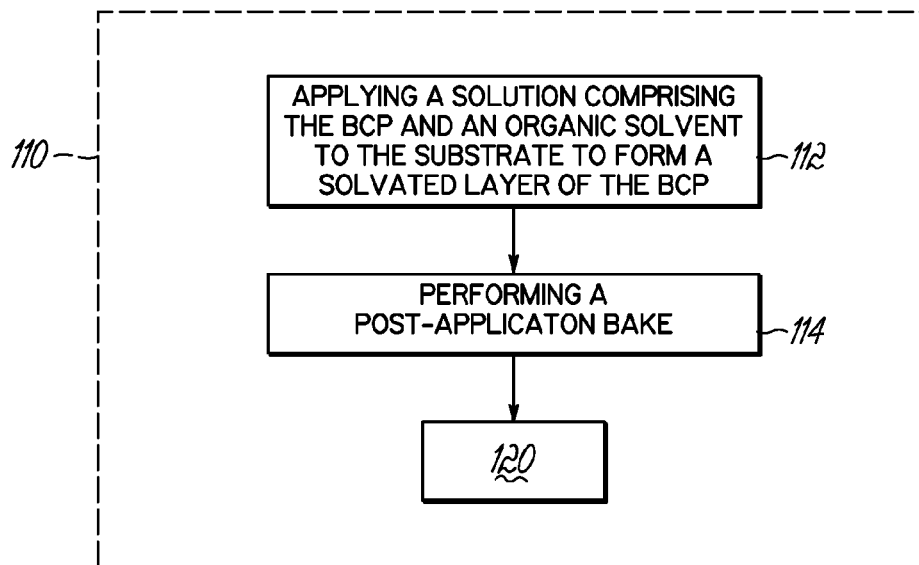


FIG. 4

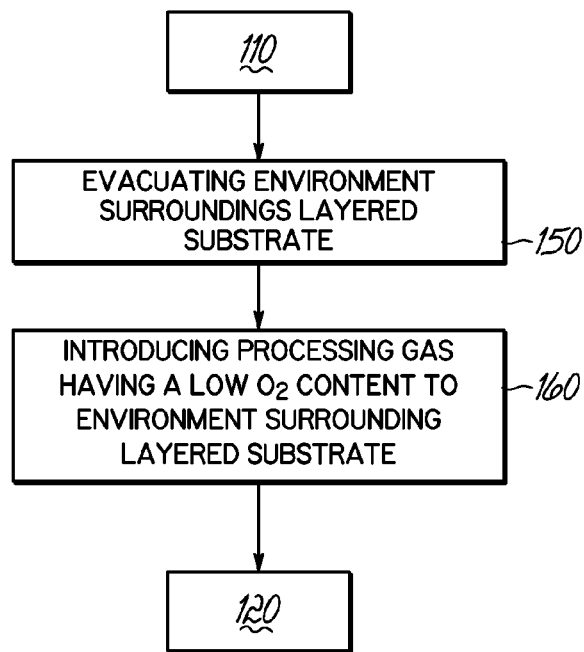


FIG. 5

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# **MULTI-STEP BAKE APPARATUS AND METHOD FOR DIRECTED SELF-ASSEMBLY LITHOGRAPHY CONTROL**

## **CROSS-REFERENCE TO RELATED APPLICATIONS**

Pursuant to 37 C.F.R. §1.78(a)(4), this application claims the benefit of and priority to prior filed co-pending Provisional Application Ser. No. 61/793,204, filed Mar. 15, 2013, which is expressly incorporated herein by reference in its entirety.

## **FIELD OF THE INVENTION**

The present invention relates generally to methods of fabricating semiconductor devices and, more specifically, to methods of fabricating semiconductor devices using directed self-assembly processes.

## **BACKGROUND OF THE INVENTION**

The need to remain competitive in cost and performance in the production of semiconductor devices has caused a continuous increase in device density of integrated circuits. To accomplish higher integration and miniaturization in a semiconductor integrated circuit, miniaturization of a circuit pattern formed on a semiconductor wafer must also be accomplished.

Design rules define the space tolerance between devices or interconnect lines so as to ensure that the devices or lines do not interact with one another in any unwanted manner. One important layout design rule that tends to determine the overall size and density of the semiconductor device is a critical dimension (CD). A critical dimension of a circuit is defined as the smallest width of a feature, e.g., a line or the smallest space between two lines. Another critical design rule is minimum pitch, which is defined as the minimum width of a given feature plus the distance to the adjacent feature edge.

The continual reduction in CDs places increasing demands on the techniques used to form the features. For example, photolithography is commonly used to pattern these features. Typically, photolithography involves passing radiation (light) through a reticle and focusing the radiation onto a radiation sensitive photoresist material. By directing radiation through the reticle, the pattern in the reticle may be focused on the photoresist. The radiation causes a chemical change in the illuminated parts of the photoresist, which allows those illuminated parts to be selectively retained or removed, depending upon whether positive or negative photoresist is used, relative to parts which were non-illuminated. Thus, the exposed (illuminated) and unexposed (non-illuminated) parts form a pattern in the photoresist.

Because photolithography is typically accomplished by projecting radiation onto a surface, the ultimate resolution of a particular lithography technique depends upon factors such as the optical proximity effects and the wavelength of the radiation used. Optical proximity effects are known to result from optical diffraction in the projection system. The diffraction causes adjacent features to interact with one another in such a way as to produce pattern-dependent variations. Accordingly, the closer together features are, the more proximity effect is seen. Thus, the ability to locate line patterns close together encroaches on optical parameter limitations.

One proposed solution for achieving critical dimensions and pitches beyond those currently achievable by photolithography techniques alone is utilizing directed self-assem-

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bly (DSA) lithography, which exploits the propensity of certain block copolymers to self-assemble into ordered morphologies, having spherical, cylindrical, lamellar, or bicontinuous gyroid microdomains. However, one challenge for incorporating DSA lithography into mass production is increased processing time caused by long annealing times required for a block copolymer to self-assemble into suitable CD targetry and uniformity.

Accordingly, new and improved methods of patterning semiconductor devices using DSA lithography are needed.

## **SUMMARY OF THE INVENTION**

Embodiments of the invention provide a method of forming a patterned substrate, the method including casting a layer of a block copolymer, having an intrinsic glass transition temperature  $T_g$ , on a substrate to form a layered substrate. The method also includes heating the layered substrate at an annealing temperature, which is greater than about 50° C. above the intrinsic glass transition temperature  $T_g$  of the block copolymer, in a first atmosphere for a first time period. The method further includes thermally quenching the layered substrate to a quenching temperature, which is lower than the intrinsic glass transition temperature  $T_g$ , at a rate of greater than about 50° C./minute in a second atmosphere. The method further includes controlling an oxygen content in the first and second atmospheres to a level equal to or below about 8 ppm to maintain the annealing temperature and the quenching temperature less than a thermal degradation temperature  $T_d$  of the block copolymer.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the general description of the invention given above, and the detailed description given below, serve to describe the invention.

FIGS. 1A and 1B are diagrammatic views of a processing system suitable for methods in accordance with embodiments of the present invention;

FIG. 2 is a flow chart illustrating a method of forming a patterned substrate, in accordance with an embodiment of the present invention;

FIG. 3 is a flow chart illustrating methods of thermally quenching the layered substrate, in accordance with an embodiment of the present invention;

FIG. 4 is a flow chart illustrating a method of casting a layer of block copolymer on a substrate, in accordance with an embodiment of the present invention; and

FIG. 5 is a flow chart illustrating a method of providing a low oxygen environment to the layered substrate prior to annealing the layer of block copolymer.

## **DETAILED DESCRIPTION OF THE DRAWINGS**

Methods for forming a patterned substrate are disclosed in various embodiments. However, one skilled in the relevant art will recognize that the various embodiments may be practiced without one or more of the specific details, or with other replacement and/or additional methods, materials, or components. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of various embodiments of the invention.

Similarly, for purposes of explanation, specific numbers, materials, and configurations are set forth in order to provide a thorough understanding of the invention. Nevertheless, the



invention may be practiced without specific details. Furthermore, it is understood that the various embodiments shown in the figures are illustrative representations and are not necessarily drawn to scale. In referencing the figures, like numerals refer to like parts throughout.

Reference throughout this specification to “one embodiment” or “an embodiment” or variation thereof means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention, but does not denote that they are present in every embodiment. Thus, the appearances of the phrases such as “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments. Various additional layers and/or structures may be included and/or described features may be omitted in other embodiments.

Additionally, it is to be understood that “a” or “an” may mean “one or more” unless explicitly stated otherwise.

Various operations will be described as multiple discrete operations in turn, in a manner that is most helpful in understanding the invention. However, the order of description should not be construed as to imply that these operations are necessarily order dependent. In particular, these operations need not be performed in the order of presentation. Operations described may be performed in a different order than the described embodiment. Various additional operations may be performed and/or described operations may be omitted in additional embodiments.

In accordance with embodiments of the present invention, the method of forming a patterned substrate is provided by utilizing a combination of a rapid annealing process and a thermal quench, which rapidly reduces the kinetics of block copolymer microphase separation to provide improved critical dimension control and reduce defects at the end of the annealing process. The method includes casting a layer of a block copolymer on a substrate; heating the layered substrate in a first environment at an annealing temperature for a first time period; and thermally quenching the layered substrate. In accordance with another embodiment, the method further includes controlling an oxygen content in the first and second atmospheres to a level equal to or below about 8 ppm to minimize the thermal degradation of the block copolymer under the annealing conditions and/or the quenching conditions.

As used herein, the term “polymer block” means and includes a grouping of multiple monomer units of a single type (i.e., a homopolymer block) or multiple types (i.e., a copolymer block) of constitutional units into a continuous polymer chain of some length that forms part of a larger polymer of an even greater length and exhibits a  $\chi N$  value, with other polymer blocks of unlike monomer types, that is sufficient for phase separation to occur.  $\chi$  is the Flory-Huggins interaction parameter and  $N$  is the total degree of polymerization for the block copolymer. According to embodiments of the present invention, the  $\chi N$  value of one polymer block with at least one other polymer block in the larger polymer may be equal to or greater than about 10.5.

As used herein, the term “block copolymer” means and includes a polymer composed of chains where each chain contains two or more polymer blocks as defined above and at least two of the blocks are of sufficient segregation strength (e.g.,  $\chi N > 10.5$ ) for those blocks to phase separate. A wide variety of block polymers are contemplated herein including diblock copolymers (i.e., polymers including two polymer

blocks (AB)), triblock copolymers (i.e., polymers including three polymer blocks (ABA or ABC)), multiblock copolymers (i.e., polymers including more than three polymer blocks (ABCD, etc.)), and combinations thereof. As used herein, the term “substrate” means and includes a base material or construction upon which materials are formed. It will be appreciated that the substrate may include a single material, a plurality of layers of different materials, a layer or layers having regions of different materials or different structures in them, etc. These materials may include semiconductors, insulators, conductors, or combinations thereof. For example, the substrate may be a semiconductor substrate, a base semiconductor layer on a supporting structure, a metal electrode or a semiconductor substrate having one or more layers, structures or regions formed thereon. The substrate may be a conventional silicon substrate or other bulk substrate comprising a layer of semiconductive material. As used herein, the term “bulk substrate” means and includes not only silicon wafers, but also silicon-on-insulator (“SOI”) substrates, such as silicon-on-sapphire (“SOS”) substrates and silicon-on-glass (“SOG”) substrates, epitaxial layers of silicon on a base semiconductor foundation, and other semiconductor or optoelectronic materials, such as silicon-germanium, germanium, gallium arsenide, gallium nitride, and indium phosphide. The substrate may be doped or undoped.

The terms “microphase segregation” and “microphase separation,” as used herein mean and include the properties by which homogeneous blocks of a block copolymer aggregate mutually, and heterogeneous blocks separate into distinct domains. In the bulk, block copolymers can self assemble into ordered morphologies, having spherical, cylindrical, lamellar, or bicontinuous gyroid microdomains, where the molecular weight of the block copolymer dictates the sizes of the microdomains formed. The domain size or pitch period ( $L_0$ ) of the self-assembled block copolymer morphology may be used as a basis for designing critical dimensions of the patterned structure. Similarly, the structure period ( $L_S$ ), which is the dimension of the feature remaining after selectively etching away one of the polymer blocks of the block copolymer, may be used as a basis for designing critical dimensions of the patterned structure.

The lengths of each of the polymer blocks making up the block copolymer may be an intrinsic limit to the sizes of domains formed by the polymer blocks of those block copolymers. For example, each of the polymer blocks may be chosen with a length that facilitates self-assembly into a desired pattern of domains, and shorter and/or longer copolymers may not self-assemble as desired.

The term “annealing” or “anneal” as used herein means and includes thermal treatment of the block copolymer so as to enable sufficient microphase segregation between the two or more different polymeric block components of the block copolymer to form an ordered pattern defined by repeating structural units formed from the polymer blocks. Annealing of the block copolymer in the present invention may be achieved by various methods known in the art, including, but not limited to: thermal annealing (either in a vacuum or in an inert atmosphere, such as nitrogen or argon), solvent vapor-assisted annealing (either at or above room temperature), supercritical fluid-assisted annealing, or laser-assisted annealing. As a specific example, thermal annealing of the block copolymer may be conducted by exposing the block copolymer to an elevated temperature that is above the glass transition temperature ( $T_g$ ), but below the thermal degradation temperature ( $T_d$ ) of the block copolymer, as described in greater detail hereinafter. Other conventional annealing methods not described herein may also be utilized.

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Turning now to the FIGS., and in particular to FIG. 1A, a processing system 10 suitable for use with embodiments of the present invention is shown. Generally, the system 10 includes a heating chamber 12 and a cooling chamber 14, each having a wafer support 16, 18 therein, configured to support and heat or cool a wafer 30 positioned thereon. The wafer support 16 also referred to as a heating plate 16, and wafer support 18 is also referred to as a chilling plate. As used herein, the wafer 30 may refer to any structure providing a “substrate” in the fabrication of one or more semiconductor devices. Each of the heating and cooling chambers 12, 14 includes an exhaust chamber 20, 22 that is fluidically-coupled to a vacuum pump (not shown) via an exhaust port 24, 26. As shown, the heating and cooling chamber may be physically isolated from one another by a movable door 31 that is operationally coupled with the operation of a transfer mechanism 32, as discussed below.

The system 10 of FIGS. 1A and 1B includes a dedicated transfer mechanism 32 positioned within the cooling chamber 14 and having a transfer arm 34 configured to transfer the wafer 30 between a home position within the cooling chamber 14, as shown in FIG. 1A and a transfer position above the heating plate 16, as shown in FIG. 1A. In this way, the wafer 30 may be transferred between the heating plate 16 and the chilling plate 18 as necessary and in accordance with a particular processing method. More specifically, the wafer 30 supported by the heating plate 16 may be heated and then lifted, via lift pins 28, off the heating plate 16. The movable door 31 may be repositioned provide an opening between the heating and cooling chambers 12, 14 to permit entry of the chilling plate 18 into the heating chamber 12. The transfer arm 34 moves the chilling plate 18 the transfer position such that the lift pin 28 may lower the wafer 30 onto the chilling plate 18. Thereafter, the transfer arm 34 withdraws the chilling plate 18 with the wafer 30 to the home position so the wafer 30 may be cooled. Although the illustrated cooling system 14 is shown with a chilling plate 18, the cooling chamber 14 may comprise at least one of a wafer chuck configured in fluid communication with a chiller unit, a thermoelectric device, or a gas inlet in fluid communication with a convective gas supply.

The system 10 may also include one or more feedback control mechanisms (not shown), such as analyzers, sensors, and controllers that monitor and adjust the atmospheres in the heating chamber, cooling chamber, and/or transfer area. For example, the feedback control mechanisms may be capable of making real-time adjustments with respect to temperature, oxygen levels, and/or pressure.

The wafer 30 may include a substrate having bottom and top hard resist layers formed thereon. While the terms “top” and “bottom” may be generally arbitrarily set, as used herein, the top of a wafer 30 is the side that is being processed or that is facing the deposition apparatus. In a preliminary step, a photoresist layer is deposited onto the top hard resist layer, patterned, and developed to provide guiding layers. In that regard, the photoresist layer may be masked, imaged, developed, and processed in accordance with conventional procedures.

With reference now to FIG. 2, a flow chart 100 illustrating a method of processing the wafer 30 according to one embodiment of the present invention is described. In step 110, a layer of block copolymer (BCP) is cast onto the substrate to form a layered substrate. The BCP has an intrinsic glass transition temperature  $T_g$ . The BCP layer includes first and second polymer blocks, which can under a thermodynamic microphase separation to form a first and a second domain. The lengths of each of the blocks making up the first and

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second polymer block may intrinsically limit the sizes of the first and second domains. For example, the first and second block copolymers may be chosen with a sufficient length to facilitate self-assembly into the desired pattern of domains because shorter copolymers may not self-assemble as desired. Exemplary first block copolymers may include, but are not limited to, poly(9,9-bis(6'-N,N,N-trimethylammonium)-hexyl)-fluorene-phenylene (“PFP”), poly(4-vinylpyridine) (“4PVP”), hydroxypropyl methylcellulose (“HPMC”), polyethylene glycol (“PEG”), poly(ethylene oxide)-co-poly(propylene oxide) di- or multiblock copolymers, poly(vinyl alcohol) (“PVA”), poly(ethylene-co-vinyl alcohol) (“PEVA”), poly(acrylic acid) (“PAA”), poly(ethyloxazoline), poly(alkylacrylate), polyacrylamide, poly(N-alkylacrylamide), poly(N,N-dialkylacrylamide), poly(propylene glycol) (“PPG”), poly(propylene oxide) (“PPO”), partially or fully hydrolyzed poly(vinyl alcohol), dextran, polystyrene (“PS”), polyethylene (“PE”), polypropylene (“PP”), polychloroprene (“CR”), polyvinyl ether (“PVE”), poly(vinyl acetate) (“PVAc”), poly(vinyl chloride) (“PVC”), polyurethane (“PU”), and polyacrylate. Exemplary second block copolymers may include, but are not limited to, silicon-containing polymers such as a polysiloxane (e.g., polydimethylsiloxane (“PDMS”)) or silicon- and iron-containing polymers (e.g., poly(ferrocenyldimethylsilane) (“PFS”)). Thus, exemplary block copolymers may include polystyrene-b-polydimethylsiloxane (“PS-PDMS”), poly(2-vinylpyridine-b-dimethylsiloxane (“P2VP-PDMS”), or polystyrene-b-poly(ferrocenyldimethylsilane) (“PS-PFS”). Modifications of the block copolymers is also envisaged, such as that disclosed in U.S. Patent Application Serial No. 2012/0046415, entitled METHODS OF FORMING BLOCK COPOLYMERS, METHODS OF FORMING A SELF-ASSEMBLED BLOCK COPOLYMER STRUCTURE AND RELATED COMPOSITIONS, the disclosure of which is incorporated herein by reference, in its entirety.

Referring still to FIG. 2, in step 120, the layered substrate is heated at an annealing temperature in a heating atmosphere for a period of time. In the annealing step 120, the layered substrate is heated to a temperature sufficient to allow the BCP to self-organize into first and second domains, each of which is characterized by its respective polymer block. This copolymer microphase separation drives lithography CD and pitch control.

Annealing of BCP's is a thermodynamic phenomenon that can be accelerated by a kinetic process. Accordingly, by raising the annealing temperature very high above the intrinsic glass transition temperature  $T_g$ , less time is required for the annealing step 120. In accordance with an embodiment, the annealing temperature may be greater than about 50° C. above the intrinsic glass transition temperature  $T_g$  of the block copolymer. The annealing temperature may be in the range of 100-400° C. With respect to a PS-PDMS block copolymer, for example, the annealing temperature may be 340° C. In accordance with an embodiment, the layered substrate may be heated in a furnace, which is adapted and designed for batch processing, or heated in an oven, which is adapted and designed for single wafer processing. The period of time may comprise a time in the range of 2 minutes to more than 4 hours.

In step 130, the layered substrate is thermally quenched in a quenching atmosphere to a quenching temperature that is less than the intrinsic glass transition temperature  $T_g$ . The cooling atmosphere may be held at room temperature, for example. The quenching rapidly lowers a temperature of the layered substrate from the annealing temperature to the quenching temperature. By quickly reducing the kinetic

movement of the polymer blocks, the CD is controlled or "locked in," which enables better CD control targeting and lowers defects. When the layered substrate is annealed at a high temperature, rapid quenching is important because the CD and pitch of the BCP continue to change as long as the temperature of the layered substrate is above the intrinsic glass transition temperature  $T_g$ . The quenching atmosphere may comprise a cooling chamber 14, specifically a cooling Front Opening Unified Pod (FOUP), for example.

According to embodiments of the present invention, thermally quenching the annealed layered substrate may be performed in several manners. For example, as shown in FIG. 3, the thermal quenching may comprise at least one of reducing a pressure of the second atmosphere (step 132), flowing convective gas around the layered substrate (step 134), contacting the layered substrate with a wafer chuck in communication with a chiller unit (step 136), and/or contacting the layered substrate with cooling arms (step 138). With respect to step 134, the convective gas may comprise nitrogen, argon, or helium, for example. The quenching may also comprise use of a thermoelectric Peltier device. The quenching step 130 may occur over a duration of time equal to or less than approximately 1-5 minutes and/or at a rate greater than or equal to 50° C./minute. With the example of PS-PDMS, the layered substrate may be quenched from a temperature of 340° C. to a temperature of 250° C. in 1 minute (i.e., at a rate of 90° C./minute).

In an embodiment in which the heating atmosphere comprises a heating chamber 12 and the quenching atmosphere comprises a cooling chamber 14, one or more lots of layered substrates may be processed simultaneously. The layered substrates may be transferred to the heating chamber 12 prior to heating the layered substrate at the annealing temperature and may be transferred to the cooling chamber 14 prior to thermally quenching. The transferring may be achieved with use of the transfer mechanism 32. By processing the layered substrates in multiple chambers, it is not necessary to wait for a single chamber to transition between a very high annealing temperature and the quenching temperature. Particularly as a result a large thermal mass inside the chamber during the processing of a batch of wafers, it takes a long time to transition between the annealing and quenching temperatures.

Use of separate heating and cooling chambers 12, 14 is efficient and enables the system 10 to maintain a high throughput. For example, layered substrates can bake in the heating chamber 12 for 60 minutes, and then proceed to the cooling chamber 14 for 30 minutes. New layered substrates may be moved into the heating chamber 12 immediately after the first lot(s) is removed to the cooling chamber 14. Therefore, productivity may be maintained without requiring time to directly heat and cool a single chamber.

In another embodiment, a single layered substrate may be positioned on a track in an oven during the heating step. Moreover, the layered substrate may be transferred from the track to the cooling chamber 14, comprising, for example, a chill plate or an oven, prior to thermally quenching. In this embodiment, the cooling chamber 14 may include at least one of a wafer chuck configured in fluid communication with a chiller unit; a convective blanket of nitrogen, argon, or helium, for example; or cooling arms. The cooling arms may be employed in a nitrogen buffer chamber.

According to one aspect of the present invention, the oxygen content of the processing environments can be controlled to minimize thermal degradation of the BCP at elevated temperatures. Returning now to FIG. 2, in a step 140, an oxygen

about 8 ppm so as to maintain the annealing temperature and the quenching temperature below a thermal degradation temperature  $T_d$  of the BCP. For the example of PS-PDMS, an oxygen level of less than 5 ppm may be required. When layered substrates are annealed at high temperatures, the polymers may oxidize, which causes CD defects. Therefore, maintaining a low oxygen environment helps prevent such oxidation and helps to lock in the CD and pitch. In an embodiment, the low oxygen environment is maintained even while the layered substrate is transferred between the chambers. After a temperature of the layered substrate is below the oxidation level of the polymer, the wafer may be transferred to atmospheric conditions, such as in a wafer FOUP.

With reference to FIG. 4, in an embodiment in which the heating chamber comprises a furnace, the casting step 110 may include applying a solution comprising the block copolymer and an organic solvent to the substrate to form a solvated layer of the block copolymer (step 112). The casting step 110 may further include performing a post-application bake of the layered substrate to reduce an amount of the organic solvent in the solvated layer (step 114) prior to heating the layered substrate at the annealing temperature. A temperature of the post-application baking is lower than the intrinsic glass transition temperature  $T_g$ . The post-application bake may be performed at a temperature of approximately 110° C., for example. The post-application bake helps to reduce the amount of casting solvent that enters the furnace and, thus, helps prevent organic build-up in the furnace. The post-application bake may be performed on a track, and the exhaust may be pumped down outside the system 10.

With reference now to FIG. 5, in an embodiment in which a single wafer is processed in an oven, the method 100 may comprise an additional step 150 of evacuating an environment surrounding the layered substrate to a pressure equal to or less than 100 torr prior to the annealing 120 of the layered substrate. The evacuation may be accomplished with use of a vacuum pump, and the resulting change in pressure may lead to a temperature decrease in the oven.

The method 100 may further comprise the optional step 160 of introducing a processing gas having an oxygen content equal to or less than about 8 ppm to the environment surrounding the layered substrate to provide the heating atmosphere, wherein the introducing the processing gas is performed after the evacuating step 150 and prior to the annealing step 120. The processing gas may comprise an organic solvent in a gaseous phase to provide a content of the organic solvent in the first atmosphere at a level equal to or greater than about 100 torr, thereby defining a solvent-rich environment.

After the annealing step 120 and the quenching step 130, the layered substrate may be maintained at a temperature below the intrinsic glass transition temperature  $T_g$ , while concurrently lowering the organic solvent content in the environment surrounding the layered substrate. This lowering of the organic solvent content may be accomplished by transferring the layered substrate to a post-application bake plate for a bake at a temperature below the intrinsic glass transition temperature  $T_g$ . This baking may help to remove an amount of residual solvent. The baking temperature should be low enough so that solvent is removed slowly, which helps to minimize polymer cracking and/or delamination of the layered substrate.

While the present invention has been illustrated by a description of one or more embodiments thereof and while these embodiments have been described in considerable detail, they are intended to restrict or in any way limit the scope of the appended claims to such detail. Additional

advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative apparatus and method, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the scope of the general inventive concept.

What is claimed is:

1. A method of forming a patterned substrate, comprising: casting a layer of a block copolymer on a substrate to form a layered substrate, wherein the block copolymer is polystyrene-b-polydimethylsiloxane, polystyrene-b-poly(ferrocenyldimethylsilane), or poly(2-vinylpyridine)-b-polydimethylsiloxane, and wherein the block copolymer has an intrinsic glass transition temperature  $T_g$ ; heating the layered substrate at an annealing temperature in a first atmosphere for a first time period, wherein the annealing temperature is greater than about 50° C. above the intrinsic glass transition temperature  $T_g$  of the block copolymer; thermally quenching the layered substrate to a quenching temperature at a rate of greater than about 50° C/minute in a second atmosphere, wherein the quenching temperature is lower than the intrinsic glass transition temperature  $T_g$ ; and controlling an oxygen content in the first and second atmospheres to a level equal to or less than about 8 ppm to maintain the annealing temperature and the quenching temperature below a thermal degradation temperature  $T_d$  of the block copolymer.
2. The method of claim 1, wherein thermally quenching comprises:
  - reducing a pressure of the second atmosphere;
  - flowing a convective gas around the layered substrate;
  - contacting the layered substrate with a wafer chuck configured in fluid communication with a chiller unit;
  - contacting the layered substrate with cooling arms; or combinations thereof.
3. The method of claim 2, wherein the thermally quenching comprises flowing a convective gas comprising nitrogen.
4. The method of claim 1, wherein the thermally quenching lowers a temperature of the layered substrate from the annealing temperature to the quenching temperature over a duration of time equal to or less than about 5 minutes.
5. The method of claim 1, wherein the oxygen content is less than about 5 ppm of oxygen.
6. The method of claim 1, wherein the first atmosphere is defined by a heating chamber and the second atmosphere is defined by a cooling chamber, the method further comprising:
  - transferring the layered substrate to the heating chamber prior to heating the layered substrate at the annealing temperature; and
  - transferring the layered substrate to the cooling chamber prior to thermally quenching.
7. The method of claim 6, wherein the cooling chamber comprises at least one of a wafer chuck configured in fluid communication with a chiller unit, a thermoelectric device, or a gas inlet in fluid communication with a convective gas supply.
8. The method of claim 6, wherein the cooling chamber comprises a cooling front opening unified pod.

9. The method of claim 1, wherein the casting of the layer of the block copolymer comprises:
  - applying a solution comprising the block copolymer and an organic solvent to the substrate to form a solvated layer of the block copolymer; and
  - performing a post-application bake to reduce an amount of the organic solvent in the solvated layer prior to heating the layered substrate at the annealing temperature.
10. The method of claim 9, wherein performing the post-application bake is performed on a track.
11. The method of claim 9, further comprising transferring the layered substrate to a furnace prior to heating the layered substrate at the annealing temperature.
12. The method of claim 1, wherein the heating the layered substrate occurs on a track in an oven, the method further comprising:
  - transferring the layered substrate from the track to a cooling chamber prior to thermally quenching.
13. The method of claim 12, wherein the cooling chamber comprises at least one of a wafer chuck configured in fluid communication with a chiller unit, a nitrogen blanket, or cooling arm.
14. The method of claim 1, further comprising:
  - evacuating an environment surrounding the layered substrate to a pressure equal to or less than 100 torr prior to the heating the layered substrate at the annealing temperature; and
  - optionally introducing a processing gas having an oxygen content equal to or less than about 8 ppm to the environment surrounding the layered substrate to provide the first atmosphere, wherein the introducing the processing gas is performed after the evacuating and prior to the heating the layered substrate at the annealing temperature.
15. The method of claim 14, wherein the processing gas comprises an organic solvent in a gaseous phase to provide a partial pressure of the organic solvent in the first atmosphere at a level equal to or greater than about 100 torr thereby defining a solvent-rich environment.
16. The method of claim 15, further comprising:
  - maintaining the layered substrate at a temperature below the intrinsic glass transition temperature  $T_g$  after thermally quenching, while concurrently lowering the organic solvent content in the environment surrounding the layered substrate.
17. The method of claim 16, further comprising:
  - transferring the layered substrate to a post application bake plate; and
  - baking the layered substrate at the temperature below the intrinsic glass transition temperature  $T_g$ , wherein the baking removes an amount of the organic solvent from the layered substrate.
18. The method of claim 1, wherein the first time period is less than about four hours.
19. The method of claim 1, wherein the first time period is about one hour.
20. The method of claim 1, wherein the block copolymer is polystyrene-b-polydimethylsiloxane, and the annealing temperature is 340° C.

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